CANADIAN JOURNAL OF RESEARCH

VOLUME 21 DECEMBER, 1943 NUMBER 12

CONTENTS

SECTION A.—PHYSICAL SCIENCES

Page

Scattering of Light by Small Drops of Water—*R. Ruedy* - - 99

INDEX, SECTION A, VOLUME 21.

SECTION B—CHEMICAL SCIENCES

Gelsemine. I. The Degradation of Gelsemine to 2 : 3-Dimethyl-indole—*L. Marion* - - - - - - - - - 247

The Reaction of Hydrogen Atoms with Propylene—*B. S. Rabinovitch, S. G. Davis, and C. A. Winkler* - - - - - - - 251

INDEX, SECTION B, VOLUME 21.

NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA

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	Annual	*Single Copy*
A and B	$ 2.50	$ 0.50
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The Canadian Journal of Research is published by the National Research Council of Canada under authority of the Chairman of the Committee of the Privy Council on Scientific and Industrial Research. All correspondence should be addressed:

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Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 21, SEC. A. DECEMBER, 1943 NUMBER 12

SCATTERING OF LIGHT BY SMALL DROPS OF WATER[1]

BY R. RUEDY[2]

Abstract

When very small drops of water increase in size until their diameter is one-fourth of the wave-length of the incident light ($2a/\lambda = 1/4$), they scatter the light essentially according to Rayleigh's law for non-conducting particles. But when the diameter increases from $\lambda/4$ to $\lambda/2$, the intensity of light scattered along directions that point toward the source decreases almost to zero, the change being most marked between $2a/\lambda = 1/4$ and $2a/\lambda = 3/8$. The sharp increase in the proportion of scattered light with an increase in size, according to the sixth power of the radius, continues however in the directions along which the main part of the scattered light is radiated by the particle. As the scattering begins to deviate from that given by Rayleigh's law, colours other than blue appear with great strength; the dispersion of the colours increases with increasing size of the particles until mainly red light remains.

Introduction

The fraction of incident light that is deflected along different directions by a small drop of water suspended in air and illuminated by a distant source depends in the first place on the state of polarization of the incident light, in the second on the ratio $2a/\lambda$ (the ratio between the diameter of the drop and the wave-length of the light), and in the third on the angle between the direction of propagation of the light wave and the direction along which the drop is examined.

When a spherical particle for which $2a/\lambda$ is not a fraction smaller than about 1/100 is illuminated by linearly polarized light, the plane x,z containing the electric vibration defines two preferred planes acting as planes of symmetry. Elliptically polarized light will be found, in general, to issue from the particle unless the line of vision is either in the plane of vibration x,z or in the plane x,y perpendicular to the direction of vibration of the incident light. If the line of vision is in the plane perpendicular to the vibration, that is, if the eye is placed in the x,y plane, the light coming from the small particle is linearly polarized, the direction of vibration being parallel to that along which the electricity oscillates in the incident ray. When the particle is observed along directions that lie in the plane of vibration of the incident light, the light seen to come from the particle is also linearly polarized, but the vibrations are parallel to the plane containing the vibration and the incident ray.

[1] *Manuscript received September 1, 1943.*

Contribution from the Research Plans and Publications Section, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1171.

[2] *Research Investigator.*

When, on the other hand, a particle, for instance, a spherical drop of water, is examined in natural unpolarized light, the direction of the incident beam defines only an axis of symmetry. In the study of the light emitted by the particle, it is assumed that the vibration of the incident light consists of two component vibrations, one of intensity $I_\perp$, at the point of observation, perpendicular to the plane containing the incident beam and the line of vision, the other, of intensity $I_\parallel$, parallel to this same plane. According to Mie (8)

$$I_\perp = \frac{\lambda^2}{4\pi^2 r^2}\, i_\perp = \frac{\lambda^2}{4\pi^2 r^2} \left| \sum_1^\infty \left(\frac{a_\nu}{\nu(\nu+1)}\, \Pi_\nu + \frac{p_\nu}{\nu(\nu+1)}\, (v\Pi_\nu - (1-v^2)\Pi'_\nu) \right) \right|^2$$

$$I_\parallel = \frac{\lambda^2}{4\pi^2 r^2}\, i_\parallel = \frac{\lambda^2}{4\pi^2 r^2} \left| \sum_1^\infty \left(\frac{a_\nu}{\nu(\nu+1)}\, (v\Pi_\nu - (1-v^2)\Pi'_\nu) + \frac{p_\nu}{\nu(\nu+1)}\, \Pi_\nu \right) \right|^2,$$

where

$$\Pi_\nu = \frac{1}{2^\nu} \sum_0^{\frac{\nu+1}{2}-1} (-1)^s \frac{(2\nu-2s)!\, v^{\nu-2s-1}}{(\nu-s)!\, s!\, (\nu-2s-1)!}\,.$$

and

$$v = \cos\gamma,$$

γ being the angle between the incident ray and the line of observation. The components of the electrical and magnetic waves issuing from the particle are designated by a_ν and p_ν (8); they depend on the index of refraction.

Influence of the Ratio $2a/\lambda$ upon the Amount of Scattered Light

When the diameter of the drop of water is only a small fraction of the wave-length, the first few terms of the sum for $i_\perp$ and $i_\parallel$ give a sufficiently accurate result, that is,

$$i_\perp = \left| \frac{a_1}{2} - \left(\frac{a_2}{2.3} - \frac{p_1}{2} \right) \cos\gamma \right|^2$$

$$i_\parallel = \left| \frac{a_1}{2} \cos\gamma - \frac{a_2}{2.3} \cos 2\gamma + \frac{p_1}{2} \right|^2$$

for a given wave-length λ and at a distance r large in comparison with the wave-length.

These expressions are of particular interest because they hold not only for spherical drops of water, but also for molecules of water, that is, they are valid when the radius is but slightly larger than 1×10^{-8} cm. Indeed, for the small value of $2a/\lambda$ that results, namely about 0.33×10^{-3}, p_1 and a_2 are both negligible, and only the terms

$$i_\perp = \frac{a_1^2}{4} \qquad\qquad i_\parallel = \frac{a_1^2}{4} \cos^2\gamma$$

remain, and their sum becomes

$$i = i_{\perp} + i_{\parallel} = \frac{a_1^2}{4}(1 + \cos^2 \gamma),$$

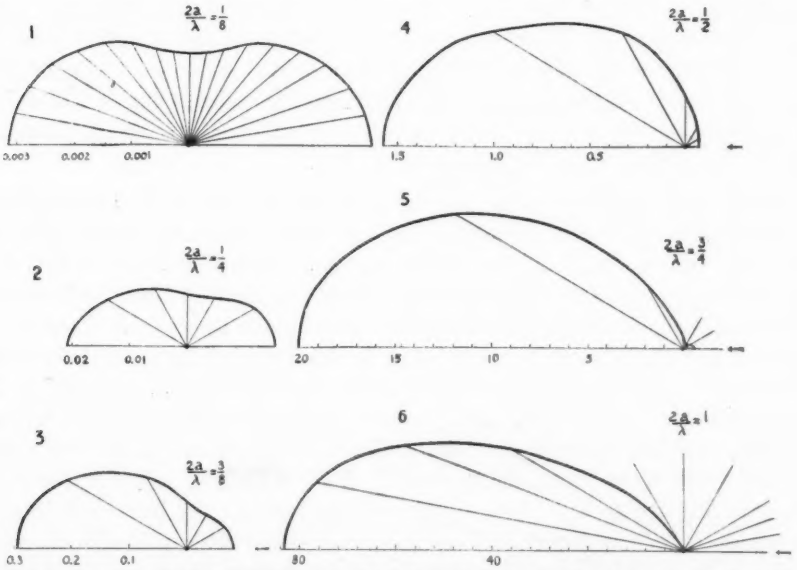
which is Rayleigh's formula for the scattering produced by molecules or non-conducting particles. Under the same conditions, the expression for a_1 can be written

$$a_1 = 2\alpha^3 \frac{m^2 - 1}{m^2 + 2} = 16 \frac{a^3\pi^3}{\lambda^3} \frac{m^2 - 1}{m^2 + 2}.$$

Hence the intensity of the diffracted radiation i is proportional to the sixth power of the radius whatever the direction along which it is observed. When, therefore, clusters of water molecules begin to unite and form small drops, the light they scatter is invisible until the intensity has exceeded the threshold of sensitivity of the eye; then the radiation appears almost suddenly, and increases rapidly in intensity with further growth of the drops. Few physical effects are known that present the same rapid change in intensity.

The calculation of the components a_1, p_1, and a_2 shows that the rapid increase in the intensity of scattered light is maintained at least until $2a/\lambda$ has increased from less than 1/1000 to about 1/10. At the two limits of this range the intensities are as $1 : 10^{12}$.

In order to ascertain the influence of the fraction $2a/\lambda$ upon the total amount of scattered light when $2a/\lambda$ exceeds 1/10, the sum of $i = i_{\perp} + i_{\parallel}$ has been



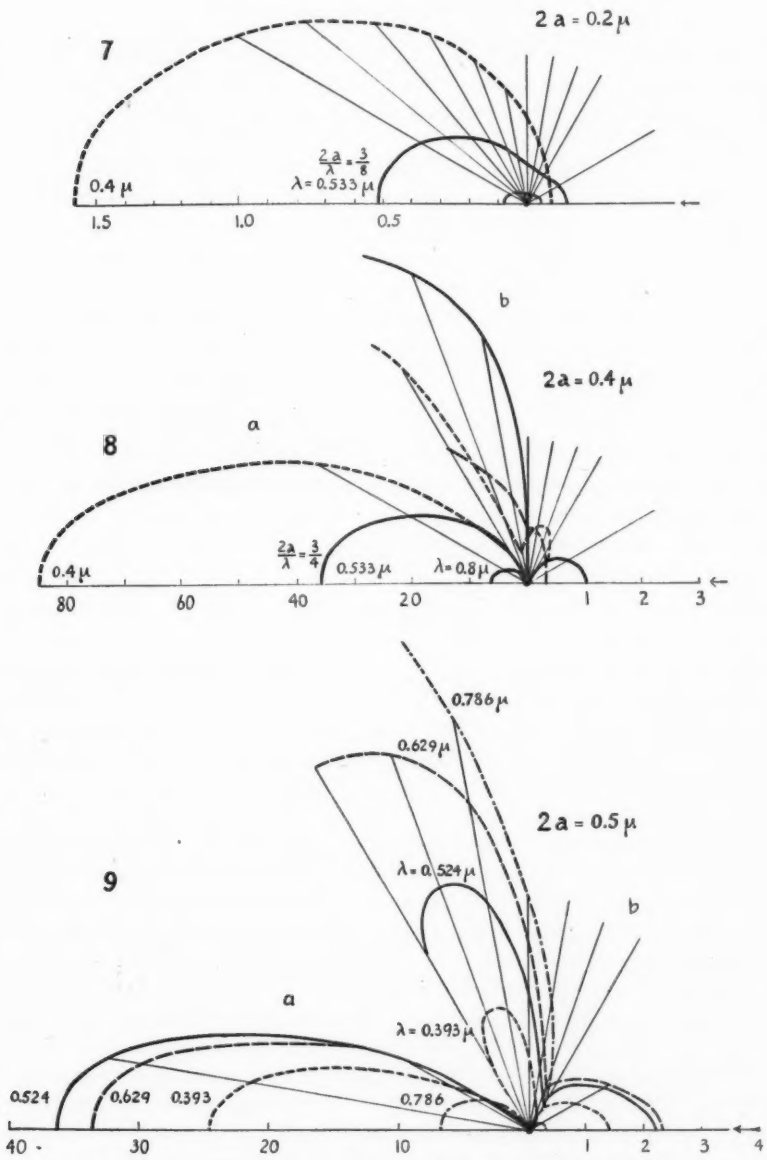
FIGS. 1 TO 6. *Radiation patterns for the light sent out by an illuminated small drop of water at various ratios $2a/\lambda$ (diameter to wave-length). The lengths represent $(i_{\perp} + i_{\parallel})$. The light source is at the right.*

calculated for spherical water particles of sizes so chosen that $2a/\lambda$ increases in steps of 1/8 from 1/8 to 1/2, and in steps of 1/4 from 1/2 to 1. The results, plotted along the directions for which they are valid, are represented in Figs. 1 to 6. Previously computed values for $2a/\lambda = 0.95$ or $2\pi a/\lambda = 3$ were used instead of those for $2a/\lambda = 1$ (1).

The graphs give the intensity of the scattered light along various directions at a distance $r = \lambda/2\pi$ from the particle when light of a single wave-length, and of unit intensity, illuminates the obstacle. Of course, no measurements are possible in a region so close to the particle, and the theory does not hold for points only a few wave-lengths distant from the drop of water. However, for distances of many wave-lengths, the actual intensities $I_|$ and $I_{||}$ are inversely proportional to the square of the distance, so that when the distance is $r = 100\lambda/2\pi$, for instance, all the intensities are only 1/10,000 of the value of $i_| + i_{||}$ shown in the graphs.

The influence of the increase in diameter on the intensity of the scattered light can be judged from the change in the scales used in plotting the various figures. Drops for which $2a/\lambda = 1/8$, or even less than 1/8, scatter according to Rayleigh's law, and deflect almost uniformly in all directions the portion of the incoming light that strikes them. When $2a = \lambda/4$ (Fig. 2), the lengths representing the intensities $i_| + i_{||}$ are slightly more than half as long as the corresponding lengths in the curve for $2a/\lambda = 1/8$, but the same length represents an intensity 100 times as great; in other words, when the radius is made twice as long, the intensity is 60 to 70 times as great. According to Rayleigh's law the intensity is multiplied by $2^6 = 64$ when the radius is doubled, and the law governing this increase holds at least approximately until the drop of water has reached a size for which $2a/\lambda = 1/4$.

As the ratio $2a/\lambda$ increases from 1/4 to 3/8, a most marked change occurs in that the particle returns less and less light back toward the source (Figs. 3 and 4). This change again is almost abrupt. Whenever $2a/\lambda = 3/4$, by far the larger portion of the scattered light is contained in the cone between 120° and 240°; for $2a/\lambda = 1$ it is confined to the cone between 135° and 225° (Figs. 5 and 6). But the suppression of the backward radiation and the concentration of the light in directions that are more nearly the continuation of the incident ray are accompanied by only a slight decrease in the rate at which the intensity increases with increasing size of the particles. Thus, the scale for the graph representing the beam of light when $2a/\lambda = 1/2$ is 30 times as great as that for $2a/\lambda = 1/4$, and the lengths used for the intensities in the beam when $2a/\lambda = 1$ and $2a/\lambda = 1/2$ are in about the same ratio, namely 33⅓. If, in addition, the differences in intensity represented by the length are considered, the sixth power law is seen to be valid approximately for the forward directions until the diameter is equal to the wave-length.



FIGS. 7, 8, 9. FIGS. 7 AND 8. *Radiation patterns ($I_1 + I_{11}$) for the light issuing from illuminated small drops of water of diameter 0.2 μ (Fig. 7) and 0.4 μ (Fig. 8) at three different wave-lengths: 0.4 μ (dashes), 0.533 μ (full line), and 0.8 μ (curves nearest to particle).* FIG. 9. *Radiation pattern for particles of 0.5 μ diameter at four different wave-lengths. In Figs. 8 and 9 the scale for the intensities along angles greater than 120° differs from that used for the smaller angles, as indicated along the zero-line below (a) or (b).*

Influence of the Wave-Length

The graphs presented illustrate at the same time the effect produced on the scattered light by a change in the wave-length of the parallel beam of light that illuminates the drop of water. Since the wave-length at the limit of the visible region in the red is about twice as long as that at the violet end of the spectrum, a change from deep red light to blue light doubles the ratio $2a/\lambda$, and changes therefore the pattern for the distribution of the light around the obstacle, rendering the angular distribution more uneven for the shorter wave-length. The change is most marked between $2a/\lambda = 1/4$ and $2a/\lambda = 1/2$, that is, when the wave-lengths in the red are equal to about four diameters, and the wave-lengths in the blue equal to twice the diameter. A particle of the corresponding size returns a considerable amount of red light back toward the source, whereas virtually all the violet light is thrown forward along the direction of propagation of the light, with the result that when seen from this side the light will appear richer in blue than it is at the source.

In order to obtain accurate results it is necessary to consider that, according to the scattering formula

$$I_{|} = \frac{\lambda^2}{4\pi^2 r^2} i_{|}(\alpha,\gamma)$$

$$I_{||} = \frac{\lambda^2}{4\pi^2 r^2} i_{||}(\alpha,\gamma),$$

the intensity at a given distance r and in a given direction from the source is proportional to the square of the wave-length and to $i_{|}$ or $i_{||}$ or their sum, depending on whether the polarized components or the total intensities are required. To find the correct intensity when the wave-length is changed so that $2a/\lambda$ increases, for instance, in steps of 1/8, it is thus not only necessary to shift from one pattern to the next (Figs. 1 to 6) but also to multiply by λ^2 the intensities valid for the new pattern. The latter operation evidently tends to produce uniform scattering of the light at all wave-lengths but is not sufficient to offset, in the entire visible region, the stronger influence of the sixth power law relating to the radius. For drops so small that $2a = \lambda/8$ at the wave-length $\lambda = 0.4\ \mu$ in the violet, the intensities $i_{|} + i_{||}$ in the extreme red, at $0.8\ \mu$, would be 1/64 of those in the violet, but since a new wave-length twice as long is involved, these intensities have to be multiplied by four, so that the intensities in the red are 1/16 of those in the violet. For larger particles, for which a change in wave-length involves a change in the pattern of light distribution, according to the scheme shown below in Table I the influence of colour is illustrated (in Figs. 7 and 8) for $2a = 0.2\ \mu$ and $2a = 0.4\ \mu$ at three different wave-lengths, $0.4\ \mu$, $0.533\ \mu$, and $0.8\ \mu$.

These values were chosen because the changes to be expected are more complex than those for smaller or larger fractions $2a/\lambda$. The wave-length in the violet was taken as unit length; this means that the distances have to be measured in multiples of $0.4\ \mu$.

TABLE I

VALUES OF $2a/\lambda$ FOR DROPS OF WATER OF DIFFERENT SIZES AND FOR THREE DIFFERENT WAVELENGTHS IN THE VISIBLE REGION

	$2a = 0.05\ \mu$	$2a = 0.1\ \mu$	$2a = 0.2\ \mu$	$2a = 0.4\ \mu$	$2a = 0.5\ \mu$
$\lambda = 0.4\ \mu$	1/8	1/4	1/2	1	5/4
$\lambda = 0.533\ \mu$		3/16	3/8	3/4	1
$\lambda = 0.8\ \mu$	1/16	1/8	1/4	1/2	
$\lambda = 1.6\ \mu$			1/8	1/4	2/3

When a drop of water having a diameter equal to $0.2\ \mu$ is illuminated by white light, waves in the red region pass near the obstacle without being appreciably disturbed, in comparison with the shorter waves, which are assumed to have at the origin the same intensity. A relatively large portion of the green light is turned back to the source so that it prevails along the small angles γ. At right angles to the beam the green light received from the particle is only half as strong as the blue light, but on account of the greater sensitivity of the eye to the green the light scattered along this direction will appear to be green rather than blue, the colour received from the smallest particle (Fig. 7).

As the diameter of the drop approaches $0.4\ \mu$ there are greater variations in the colours (Fig. 8). In the light that returns from the particle toward the source, green predominates again. At approximately 90° to the beam, red accounts now for the larger part of the intensity, at a slightly greater angle orange is strongest, then green; but blue is rapidly increasing and prevails more and more as the line of vision is rotated about the drop beyond the direction at which the angle γ is 120° until it points towards the source.

For still larger particles, with a diameter equal to $0.5\ \mu$, the different colours are spread out through wider angles (Fig. 9 drawn according to Blumer's calculations (1)). Red at $0.786\ \mu$ ($2a/\lambda = 0.637$) exceeds orange, green, and violet in intensity between $\gamma = 80°$ and $\gamma = 120°$; orange at $0.629\ \mu$ ($2a/\lambda = 0.795$) is the strongest of the four colours when the drop of water is examined at angles γ between 135° and 150° with reference to the incident ray, while green, at $0.524\ \mu$ ($2a/\lambda = 0.955$), becomes predominant for larger angles. In contrast with the scattering by much smaller drops, blue is no longer found to exceed or equal in strength any of the other colours, not even along the direct continuation of the incident beam. As this dispersion of the colours continues when $2a/\lambda$ increases, red and orange become the main constituents of scattered light.

Polarization of the Scattered Light

The two components, $i_\perp$ and $i_\parallel$, whose sum represents the intensity of the scattered light have in general very unequal values. For the smallest drops $i_\parallel$ vanishes so that the electrical vibration of the scattered light occurs

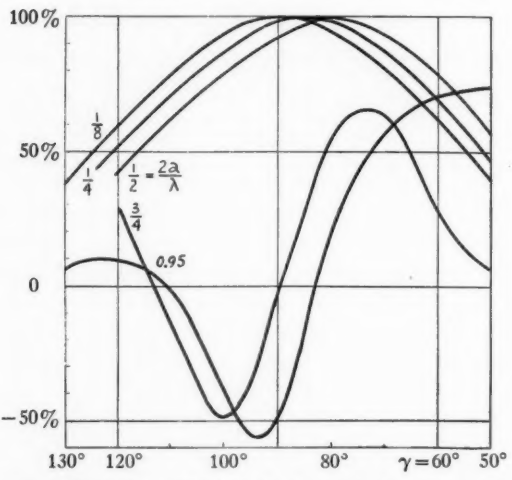


FIG. 10. *Degree of polarization of light issuing from a drop of water when it is illuminated by unpolarized light. Vibrations perpendicular to the plane passing through the incident beam and the line of sight are given a positive sign; vibrations parallel to this plane are distinguished by the negative sign.*

exclusively along the direction perpendicular to the plane containing the incident ray and the line of vision, although unpolarized light is used for illuminating the drop. When $2a/\lambda$ is at least 1/8, however, the component $i_{||}$ is appreciable, and the scattered light is therefore only partially polarized. It is convenient to express the degree of polarization by the fraction $(i_{|} - i_{||})/(i_{|} + i_{||})$. The electrical vector of the more abundant component of the light is then perpendicular to the plane of observation when the fraction is positive, and it is parallel to this plane, which passes through the incident ray and the line of observation, when the fraction is negative. The degree of polarization varies for each value $2a/\lambda$ with the angle γ (Fig. 10). The change is symmetrical when $2a/\lambda$ does not exceed 1/8. At points in the plane of the beam the light is completely polarized for $\gamma = 90°$. The degree of polarization is decreased by the same amount when the direction of observation is altered so as to be situated either closer to the source or closer to the straight line followed by the incident beam after it has encountered the particle. Complete polarization for $\gamma = 90°$ at right angles to the beam is the rule until the diameter of the drop has increased to $\lambda/2$, but after $2a/\lambda$ has exceeded 1/8, the variations are no longer symmetrical with respect to $\gamma = 90°$ when the direction of observation is rotated either toward the source or through the same angle away from the source. The degree of polarization is reduced more rapidly through the region farther away from the source, that is, for angles exceeding 90°, than it is in the region closer to the source of light.

When the diameter exceeds $\lambda/2$, complete polarization is obtained at 80° instead of at 90°; for still larger values of $2a/\lambda$, the maximum shifts to still

smaller angles, to 70° for $2a/\lambda = 3/4$, and to 60° for $2a/\lambda = 1$. When this shift takes place, complete polarization is no longer obtained at any angle.

For $2a/\lambda = 3/4$ the parallel component is for the first time stronger than the vertical component. With still larger fractions positive and negative peaks occur.

Practical Application

From a knowledge of the degree of polarization alone it would be difficult to decide whether one is dealing with drops of water for which $2a/\lambda = 1/8$, or 1/4, or 3/8. Through the range $2a/\lambda = 1/2$ to $2a/\lambda = 1$, however, the change in polarization for angles between 120° and 150° is so rapid that its study should enable the observer to determine the size of the particles.

Complete polarization at $\gamma = 90°$ is no proof that the particles are extremely small; their diameter may be an appreciable fraction, 1/8 to 3/8, of the wave-length. It is necessary to study the distribution of the scattered light before any valid conclusion regarding the size can be drawn. Absence of polarization at $\gamma = 90°$ on the other hand, indicates that the diameter of the particle is at least equal to one-half wave-length.

Studies of the changes in the state of polarization of the light lead also to a correct determination of the size of the drops formed in a steam jet when condensation is brought about by blowing vapours of hydrochloric acid against the jet; this is the method described by Helmholtz for the production of coloured steam.

On illuminating such steam jets through a glass filter that transmits only violet and dark red rays from an electric arc, it is found that the red light scattered at right angles to the beam is completely polarized but not the blue nor the violet (2).

According to the calculations presented above, the red light observed at right angles possesses no preferred direction of vibration when the diameter, $2a$, of the drops is equal to $3/4\ \lambda$, but it is completely polarized when the diameter is smaller than half the wave-length (Fig. 10).

Such conditions must obtain in the coloured steam jet described (2) when the radius of the drops is equal to 0.15 μ. (The original, necessarily rough, determinations by means of the diffraction rings appearing as coloured halos or coronas when point sources are viewed through fogs or clouds give 0.46 μ for the radius; however, it is now known that the corona method is not applicable to drops with a diameter much smaller than 20 μ (10) .)

When the stream of ions supplied by the acid vapours is gradually increased in strength, the colour of the jet observed in diffuse light against a dark background turns from reddish yellow to yellow, then to yellowish blue, and finally to blue. The change in colour indicates that, as is to be expected, smaller and smaller water drops are being formed when the centres of condensation are more numerous.

After the size of the particles, assumed to be uniform, has been ascertained, it is possible to determine their concentration, in the air, either by measuring

the attenuation of the beam—when the particles are more or less opaque—or by studying the amount of light scattered at right angles—when the particles are transparent and true absorption is negligible in comparison with scattering.

True absorption and scattering are both proportional to the number of particles that are contained in unit volume. Let it be assumed that the steam in a cube of 1 cm. sides be examined at right angles to the incident beam, that is, through one of the lateral faces of the cube. At the distance r, the beam after having been scattered by the water droplets and sent along this direction has for $\lambda = 0.55\ \mu$ an intensity that is a fraction

$$N(i_| + i_{||})\lambda^2/4\pi^2r^2 = 0.0122\ N(i_| + i_{||})/r^2$$

of that of the incident light. (The total area, $N\pi a^2$, of the droplets contained in each cubic centimetre of the steam must not exceed unity in order to guard against overlapping of the cross-sections.) It is difficult to state what is the lowest intensity that the beam may have and still be rendered visible by scattered light under laboratory conditions, but a lower limit for its brightness, and therefore for the number N, may be set by considering the radiation scattered by the same volume of dry steam.

When a beam of unpolarized light of intensity i_λ erg per sq. cm. at the wave-length λ passes through a gas or vapour that has the refractive index m and contains N molecules per cc., the intensity of the light scattered at an angle γ to the beam is given by the expression:

$$\frac{i_{s\lambda}}{i_\lambda} = \frac{2\pi^2(m-1)^2(1+\cos^2\gamma)}{N\lambda^4}\ .$$

For steam at the pressure p and the temperature t the index of refraction $m_{t,p}$ is given by:

$$m_{t,p} - 1 = \frac{d_{t,p}}{d_{0,760}}\ (m_0 - 1)\ ,$$

where m_0 is the index the substance would have if at 0° C. there would be the same number of molecules per cubic centimetre as in hydrogen at 0° C. and 760 mm. of mercury (4, 6). For the green line of mercury at $0.546\ \mu$

$$m_0 - 1 = 253 \times 10^{-6}\ .$$

At the temperature and pressure at which the expansion of steam is studied in convergent-divergent nozzles, the density $d_{t,p}$ (0.776 kg. per cu. m. at 108° C., 0.661 kg. per cu. m. at 103° C.) differs but little from the value $d_{0,760}$ (namely 0.804 kg. per cu. m.) so that $(m-1)$ may be taken as approximately equal to 253×10^{-6}. Hence at $\gamma = 90°$ and for $\lambda = 0.55\ \mu$ the intensities of the scattered and the incident beams are in the ratio

$$\frac{i_{s,\lambda}}{i_\lambda} = \frac{1.26 \times 10^{-6}}{2.687 \times 10^{19}\ \lambda^4} \approx 10^{-8}\ .$$

Experience has shown that in dry steam the scattered light is distinctly visible (11). This agrees with what is known about the visibility threshold. Projection of the light from an electric arc by the usual methods furnishes a

parallel beam of about 100 to 700 lumen per sq. cm. (3). From many tests it can be concluded that an area subtending an angle of 10° or more at the eye becomes visible when its brightness exceeds 10^{-9} lambert, or about 10^{-9} lumen per sq. cm. of a perfectly diffusing surface (5). The illumination provided by light scattered from an arc is, therefore, more than sufficient to render dry steam visible. It is at the same time less intense than the beam that a much smaller number N of water droplets are able to provide when their diameter approaches the wave-length of light.

It may be pointed out in conclusion that since with the larger particles the scattered light appears mainly as a continuation of the incident beam (Figs. 7 to 9) the attenuation factor will be reduced to a value smaller than the theoretical amount, $2N\pi a^2$, obtained on the assumption that the scattered light is uniformly distributed in all directions (8).

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* *Previous articles are listed in the report by R. Ruedy, Vision at night, Ottawa, 1942, N.R.C. No. 1041.*

CANADIAN JOURNAL OF RESEARCH

VOLUME 21
1943

SECTION A

CANADA

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SECTION A

INDEX TO VOLUME 21

Authors

Clark, A. L. and Katz, L.—The resonance method of measuring the ratio of the specific heats of a gas, C_p/C_v. Part IV., 1.

Davidson, R. R.—See King, R. O.

Feeny, H.—See Giguère, P. A.

Gauvin, W. and Winkler, C. A.—Effect of surface on cathode polarization during the electrodeposition of copper, 37.

Giguère, P. A. and Feeny, H.—The magneto-optic rotation of hydrogen peroxide, 69.

Grasham, W. E.—See Keevil, N.B.

Griffith, L.—A theory of the size distribution of particles in a comminuted system, 57.

Katz, L.—See Clark, A. L.

Keevil, N. B. and Grasham, W. E.—Theory of alpha-ray counting from solid sources, 21.

King, R. O. and Davidson, R. R.—Liquid flow at small constant rates, 65.

Ruedy, R.—Absorption of light by small drops of water, 79.
Scattering of light by small drops of water, 99.

Stansfield, E.—Humidity data expressed in grains water vapour per pound of dry air, 51.

Tessier, H.—See Woodcock, A. H.

Watson, J. H. L.—Applied electron microscopy, 89.

Winkler, C. A.—See Gauvin, W.

Woodcock, A. H. and Tessier, H.—A laboratory spray drier, 75.

SECTION A

INDEX TO VOLUME 21

Subjects

Absorption
of light by
small drops of water, 79.
steam flowing through nozzles, 80, 107.
of α-rays by solid deposits, Theory of, 21.

Air, Dry, Humidity data expressed in grains water vapour per pound of, 51.

Aloe arborescens, Examination of wall structure of mesophyll of, with electron microscope, 96.

Alpha-rays, See α-Ray.

Antirrhinum majus L. var. Rosalie, Examination of cuticle of leaf of, with electron microscope, 95.

Argon, Ratio of specific heats of, at 24.2° C., 11.

Botany, Application of electron microscope to botanical investigations, 95.

Camera, Electron diffraction, Use of electron microscope as, 93.

Carbon dioxide, Ratio of specific heats of, at 23.8° C., 12.

Cathode polarization during electrodeposition of copper, Effect of surface on, 37.

Comminuted system, A theory of the size distribution of particles in a, 57.

Copper, Electrodeposition of, Effect of surface on cathode polarization during, 37.

Cuticle, Leaf, Examination of, with electron microscope, 95.

Diffraction camera, Electron, Use of electron microscope as, 93.

Dispersion of magnetic rotation of hydrogen peroxide and water, 73.

Distribution, Size, of particles in a comminuted system, A theory of, 57.

Drier, Spray, A laboratory, 75.

Drying of food, A laboratory spray drier for, 75.

Dust, See Mine dust.

Egg, Dried, A laboratory spray drier for the production of, 75.

Electrodeposition of copper, Effect of surface on cathode polarization during, 37.

Electrolysis, See Electrodeposition of copper.

Electron diffraction camera, Use of electron microscope as, 93.

Electron microscope
Applications of, to botanical investigations, 95.
Examination of mine dust with, 91.
Stereoscopic photography with, 89.
Use of, as an electron diffraction camera, 93.

Electron microscopy, Applied, 89.

Emitters, α-Ray,
Data for, 27.
Theory of α-ray counting from, 21.

Flax fibres, Broken, Stereoscopic views of, taken with electron microscope, 97.

Flow
Liquid, at small constant rates, 65.
Scattering and absorption of light by steam flowing through nozzles, 80, 107.

Gases, Specific heats of, C_p/C_v, Resonance method of measuring ratio of, 1.

Gasoline, Octane ratings, Humidity data charts for use in determination of, 52, 53.

Granite, Test with, of theory of α-ray counting from solid sources, 35.

Grinding, A theory of the size distribution of particles in a comminuted system, 57.

Haring cell, Method for obtaining reproducible cathode-polarization–current-density curves with, 37.

Heat, See Specific heats.

Helium, Ratio of specific heats of, at 23.1° C., 15.

Humidity data, expressed in grains water vapour per pound of dry air, 51.

Hydrogen, Ratio of specific heats of, at 24.4° C., 13.

Hydrogen peroxide
Magneto-optic constants of, 71.
Magneto-optic rotation of, 69.

Leaf cuticle, Examination of, with electron microscope, 95.

Light,
Absorption of
by salt solutions, 83.
by small drops of water, 79.
by water, 82.
Scattering and absorption of, by steam flowing through nozzles, 80, 107.
Scattering of, by small drops of water, 99.

Liquid flow at small constant rates, 65.

Magnetic rotatory power of aqueous solutions of hydrogen peroxide at 10° C., 72.

Magneto-optic rotation of hydrogen peroxide, 69.

Mesophyll of Aloe arborescens, Examination of wall structure of, with electron microscope, 96.

Microdoser, Rideal
Type A, 65.
Type B, 66.

Microscopy, Electron, Applied, 89.

Milk, Dried, A laboratory spray drier for the production of, 75.

Mine dust, Particle sizes in, examined with electron microscope, 91.

Molecular magnetic rotation of hydrogen peroxide, 71.

Nitrogen, Ratio of specific heats of, at 23° C., 12.

Nozzles, Scattering and absorption of light by steam flowing through, 80, 107.

Octane ratings of gasoline, Humidity data charts for use in determination of, 51.

Particle(s)
sizes in mine dust, examined with electron microscope, 91.
A theory of the size distribution of, in a comminuted system, 57.

Photography, Stereoscopic, with the electron microscope, 89.

Plants, Examination of, with electron microscope, 89.

Polarization, Cathode, Effect of surface on, during electrodeposition of copper, 37.

Polarization of light scattered by small drops of water, 105.

Pressure
Mean instantaneous, in resonance method of measuring ratio of specific heats of a gas, Fundamental equation for, 2.
Ratio of specific heats of a gas as a function of, 11–16.

Radioactivity, Theory of α-ray counting from solid sources, 21.

α-Ray
absorption data for a number of minerals, 26.
counting from solid sources, Theory of, 21.
emitters, Data for, 27.

Refractive index (magneto-optic constant) of hydrogen peroxide, 71.

Resonance method of measuring the ratio of the specific heats of a gas, C_p/C_v, IV, 1.

Rideal microdoser
Type A, 65.
Type B, 66.

Rocks, α-Ray emission from, 30.

Rotation, Magneto-optic
constant of hydrogen peroxide, 71.
of hydrogen peroxide, 69.

Salt solutions, Absorption of light by, 83.

Scattering of light
by small drops of water, 99.
by steam flowing through nozzles, 80, 107.

Size distribution of particles in a comminuted system, A theory of, 57.

Specific heats of a gas, C_p/C_v, Resonance method of measuring ratio of, 1.

Spray drier, A laboratory, 75.

Steam
flowing through nozzles, Scattering and absorption of light by, 80, 107.
jets, Coloured, Use of, in determination of size of drops of water in a steam jet, 107.

Stereoscopic photography, with the electron microscope, 89.

Temperature change in resonance method of measuring ratio of specific heats of a gas, 4.

Verdet constant of hydrogen peroxide, 71.

Wall structure of mesophyll of Aloe arborescens, Examination of, with electron microscope, 96.

Water
Absorption of light by
small drops of water, 79.
water, 82.
Scattering of light by small drops of, 99.
vapour, Humidity data expressed in grains of, per pound of dry air, 51.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 21, SEC. B. DECEMBER, 1943 NUMBER 12

GELSEMINE

I. THE DEGRADATION OF GELSEMINE TO 2 : 3-DIMETHYL-INDOLE[1]

BY LÉO MARION[2]

Abstract

The alkaloid gelsemine was degraded with selenium and with soda lime to mixtures of bases and neutral products. The latter, from either degradation, contained a fraction identified as 2 : 3-dimethyl-indole.

Gelsemine, the chief alkaloid present in the root of *Gelsemium sempervirens* Ait, has been assigned the formula $C_{20}H_{22}O_2N_2$ by Moore (3). It crystallizes from acetone with one molecule of solvent of crystallization, which is driven off at 120° C. It is known to contain one non-phenolic hydroxyl but no methoxyl group. Chu and Chou have found that the alkaloid can be hydrogenated catalytically to dihydrogelsemine (2) and that it forms a dibromo-derivative which, when dissolved in acid and precipitated with sodium carbonate, loses hydrogen bromide (1).

A determination of the methylimino-group showed that one such group is present in the molecule.

When a small quantity of the base was fused with a pellet of potassium hydroxide and the cooled melt extracted with ether, the extract yielded an oil that produced a very strong coloration in Ehrlich's test. This suggested distillation with soda lime as a means of degradation. Upon such treatment, gelsemine yielded a mixture of bases and neutral substances. The bases formed crystalline picrates, but these were obtained in quantities insufficient for identification.

The neutral portion of the product was fractionated by distillation *in vacuo*. One fraction had a strong fecal odour and, when treated with picric acid, it formed a bright red picrate. This picrate was identified as 2 : 3-dimethyl-indole picrate by analysis and by melting point and mixed melting point with an authentic specimen synthesized from phenylhydrazine and methyl ethyl ketone.

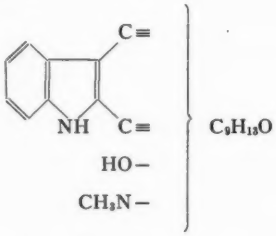
Degradation of gelsemine with selenium also produced a small quantity of the same indole derivative, isolated and identified as the picrate.

[1] *Manuscript received August 17, 1943.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1163.

[2] *Chemist.*

The indole nucleus must, therefore, be present in the gelsemine molecule, which can now be expanded to



Furthermore, the isolation by Chou and Chu (1, 2) of a dihydro- and a dibromo-derivative of gelsemine indicates the presence of a double bond in the $C_9H_{13}O$ moiety.

Experimental

The gelsemine used in the following experiments was obtained from the root of *Gelsemium sempervirens* Ait.

The alkaloid was crystallized repeatedly from boiling acetone, from which it separated in colourless prismatic needles containing one molecule of solvent of crystallization, m.p. 179° C.* A sample was heated for one hour at the temperature of boiling xylene in an Abderhalden gun and analysed. Calc. for $C_{20}H_{22}O_2N_2$: C, 74.52; H, 6.83; N, 8.70; imino–CH_3, 4.65%. Found: C, 74.89, 74.94; H, 6.80, 6.83; N, 8.79; imino–CH_3 , 5.16%.

Distillation of Gelsemine with Soda Lime

Into a glass tube, sealed at one end and bent at an angle of 135°, was introduced finely ground soda lime (2 gm.) and then a ground mixture of gelsemine (2 gm.) and soda lime (5 gm.). This was covered with more soda lime (about 20 gm.). The tube was placed in an electrically heated furnace and connected to a receiving flask. It was gradually heated to 320° C. and kept at that temperature for eight hours. In the course of the experiment, a thick oil slowly distilled into the receiver. Three such runs were carried out and the distillates combined. The contents of the tubes was extracted in a Soxhlet with ether and the extract combined with the distillates.

The resulting ether solution was extracted with several portions of dilute hydrochloric acid (1 : 1). The combined acid extract was filtered through charcoal, basified with strong potassium hydroxide, and the precipitated base collected in ether. The solvent was distilled off and the residual oil fractionated *in vacuo*. A light oil distilled at 130 to 140° C. (<1 mm.) and a very thick oil at 160 to 200° (<1 mm.), leaving an appreciable undistilled residue. The lower boiling oil was dissolved in methanol and treated with a methanolic solution of picric acid. On standing, a picrate crystallized out; this was recrystallized from a little boiling methanol. It separated in small yellow

* *All melting points are corrected.*

warts, m.p. 210° after sintering somewhat at 202°. Insufficient material was available for further purification. Found: N, 12.35%.

The thick oil, b.p. 160 to 200° C. (<1 mm.), formed a very insoluble picrate, which was recrystallized from boiling acetone, from which it separated as small yellow prisms, m.p. 238° (decomp.) with previous shrinking. Found: N, 13.97%.

Isolation of 2 : 3-Dimethyl-indole

The original ether solution, which had been extracted with dilute hydrochloric acid, was washed with water, dried over sodium chloride and distilled on the steam-bath. The residual oil gave a strong coloration in the Ehrlich test. It was fractionated *in vacuo* and a fraction obtained which, when redistilled, boiled at 97° (1 mm.). Wt., 74 mg. This distillate had a pronounced fecal odour. It was dissolved in a little absolute ether and poured into a solution of picric acid in absolute ether. A picrate separated at once as dark red needles, which, after one recrystallization from a mixture of absolute ether and petroleum ether, melted at 153°. Calc. for $C_{16}H_{14}O_7N_4$: C, 51.34; H, 3.74; N, 14.97%. Found: C, 49.79, 50.56; H, 3.89, 4.36; N, 14.87%. In admixture with an authentic specimen of 2 : 3-dimethyl-indole picrate (m.p., 157°) it melted at 155°.

Degradation of Gelsemine with Selenium

Gelsemine (2 gm.) was mixed with black selenium (2 gm.) in a small flask carrying a column, about 40 cm. long, at the top of which was a side-arm connected to a downward condenser extending into a receiving flask. Through a capillary tube extending into the column a stream of nitrogen was kept sweeping throughout the experiment. After the air had been displaced, the flask was lowered into a metal bath and the temperature gradually brought up to 320° C., where it was kept for three hours. An oil was produced which refluxed in the column and distilled over. Two more such runs were made, and the distillates combined and dissolved in ether. The ether solution was washed with dilute (1 : 1) hydrochloric acid, with aqueous sodium hydroxide and with water. After drying over sodium chloride the ether solution was distilled and the residual oil (positive Ehrlich test) fractionated *in vacuo*. A straw-coloured oil, b.p. 110 to 120° C. (2 mm.) (wt. 50 mg.) was obtained and a thick oil, b.p. 200° (2 mm.). The lower boiling fraction formed a picrate obtained as red needles after recrystallization from ether–petroleum-ether, m.p. 154 to 155° C. This was identical with 2 : 3-dimethyl-indole picrate obtained from the soda lime degradation and with a synthetic specimen.

Synthesis of 2 : 3-Dimethyl-indole

To phenylhydrazine (21.6 gm.) in a Claisen flask was added gradually, with cooling, methyl ethyl ketone (16 gm.). The liquid, which became turbid, was allowed to stand for one hour and fractionated. The fraction boiling at 146° (16 mm.) was collected. Wt., 23 gm. Yield, 71%. Fused and ground zinc chloride (27.3 gm.) was added to the distillate, which was

heated over a bare flame until the exothermic reaction started. The reaction mixture was allowed to stand for one hour and steam-distilled. The indole was extracted from the distillate with ether, the extract dried, and the ether distilled off. The crystalline residue was distilled *in vacuo*, b.p. 132 to 133° (1 mm.). The distillate (wt., 17.6 gm.) was recrystallized several times from methanol–ether and from ether–petroleum-ether, m.p. 108°. Some of the 2 : 3-dimethyl-indole was converted to the picrate. This, after recrystallization from ether–petroleum-ether, was obtained as red needles, m.p. 157°.

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THE REACTION OF HYDROGEN ATOMS WITH PROPYLENE[1]

By B. S. Rabinovitch[2], S. G. Davis[3], and C. A. Winkler[4]

Abstract

The reaction of hydrogen atoms with propylene has been studied by the Wood–Bonhoeffer method over the temperature range 30 to 250° C. The principal products are propane, ethane, and methane. No unsaturated products were isolated. The nature and proportions of products are independent of temperature. A mechanism is suggested, based on the formation of an active propyl radical as the primary step.

Introduction

The reactions of hydrogen atoms with lower saturated hydrocarbons have been extensively studied, but similar investigations with the corresponding unsaturated compounds have been confined almost exclusively to ethylene. The reaction of hydrogen atoms with propylene appeared to be of particular interest because the structure of the molecule allows of the reactions of both saturated and unsaturated compounds. A note by Moore and Taylor (8) on the mercury photosensitized reaction of hydrogen and propylene has already appeared. The present paper gives the results of an investigation of this reaction by the Wood-Bonhoeffer method.

Experimental

Propylene was prepared by dehydration of isopropyl alcohol in the presence of phosphoric acid (1). The material was purified by repeated distillation between two traps, the final product showing no impurities by the analytical methods employed in the study.

Commercial hydrogen was purified by passing it through a silica tube containing platinized asbestos heated to 500° C., and then through a silica gel trap maintained at liquid air temperature. The hydrogen was moistened by passing it over water before it was admitted to the apparatus.

The apparatus and procedures were similar in all essentials to those described in earlier communications from this laboratory (10, 16).

Products were separated by distillation on a low temperature column of the Podbelniak type, and checked by combustion. The "C_3" fraction was analysed for saturate–olefine ratio in a Burrell gas analysis apparatus.

[1] *Manuscript received August 13, 1943.*
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que.
[2] *Postgraduate student and holder of a Fellowship under the National Research Council of Canada.*
[3] *Postgraduate student and holder of a Canadian Industries Limited Fellowship.*
[4] *Assistant Professor of Chemistry.*

Results

The experimental data are recorded in Tables I and II. Slight loss of product, probably methane, appears to have occurred, but is not important for the discussion of the results. The products were carefully examined for ethylene and acetylene by qualitative tests as well as distillation, but neither gas was present.

TABLE I

EXPERIMENTAL DATA FOR THE REACTION OF HYDROGEN ATOMS WITH PROPYLENE

Pressure = 0.35 mm.

Run No.	Temp., °C.	Propane flow, moles/sec. × 10^6 (N.T.P.)	Hydrogen flow, moles/sec. × 10^6 (N.T.P.)	Atom concn., %	Propylene reacted, %	Reaction products—Moles/mole propylene reacted			
						CH_4	C_2H_6	C_3H_8	"C_4"
1	30	4.50	19.6	14.0	45.6	0.41	0.64	0.38	<0.01
2	30	4.50	19.6	14.0	44.1	0.47	0.64	0.33	<0.01
3	100	4.50	19.6	12.2	41.5	0.49	0.71	0.29	<0.01
4*	100	4.50	19.6	12.2	43.9	0.52	0.66	0.32	<0.01
5	100	4.50	19.6	12.2	41.6	0.46	0.71	0.31	<0.01
6	170	4.50	19.6	10.1	38.8	0.43	0.73	0.31	<0.01
7	170	4.50	19.6	10.1	39.0	0.39	0.70	0.34	<0.01
8	170	4.50	19.6	10.1	39.1	0.42	0.68	0.34	<0.01
9	250	4.50	19.6	8.3	39.5	0.46	0.68	0.33	<0.01
10	250	4.50	19.6	8.3	38.1	0.47	0.65	0.32	<0.01
11	54	1.10	19.6	~14.0	100	1.43	0.76	Trace	Trace

* *A trace of ethylene was found.*

TABLE II

MEAN VALUES OF PRODUCTS

Temp., °C.	Propylene, reacted, %	Reaction products—Moles/mole C_3H_6 reacted			
		CH_4	C_2H_6	C_3H_8	"C_4"
30	44.9	0.44	0.64	0.35	<0.01
100	42.3	0.49	0.69	0.31	<0.01
170	39.0	0.41	0.70	0.33	<0.01
250	38.8	0.46	0.67	0.33	<0.01
54	100	1.43	0.76	Trace	Trace

The collision numbers, yields, and activation energies are recorded in Table III. The diameter of the propylene molecule was taken as 4.10×10^{-8} cm. (15), and the diameter of the hydrogen atom as 2.14×10^{-8} cm. (2). A steric factor of 0.1 was assumed in obtaining the activation energy. Calculations were made in the usual way and need not be detailed.

TABLE III

DATA FOR THE CALCULATION OF COLLISION YIELDS AND ACTIVATION ENERGIES EMPLOYING MEAN VALUES

Temp., °C.	Total flow corrected for presence of atoms, moles/sec. $\times 10^5$	Reaction time, sec.	Partial pressure hydrogen atoms, mm.	$Z_{C_3H_6 \cdot H}$ in reaction time $\times 10^{-5}$	Reaction % Mean	Over-all collision yield $\times 10^6$	E ($A = 0.1$)
30	2.56	0.668	0.0404	4.81	44.9	0.918	7.0
100	2.54	0.547	0.0352	3.09	42.3	1.63	8.3
170	2.52	0.465	0.0290	2.01	39.0	1.95	9.6
250	2.50	0.393	0.0238	1.33	38.8	2.92	10.8

Discussion

The following are the more striking features of the experimental results:

(*a*) Large amounts of ethane were produced at room temperature.

(*b*) Ethylene was not isolated at any temperature.

(*c*) The nature and proportions of the reaction products were virtually independent of temperature.

(*d*) The extent of reaction exceeded the available concentration of hydrogen atoms.

A quantitative explanation of the results is not possible, but a suggested course of reaction is discussed in a general way.

The Primary Step

Possible primary reactions are:

$$C_3H_6 + H \longrightarrow C_3H_7 \qquad (1)$$

$$\longrightarrow CH_2{-}CH{=}CH_2 + H_2 \qquad (2)$$

$$\longrightarrow CH_4 + C_2H_3 . \qquad (3)$$

Moore and Taylor (8) found propane, as in the present study, and hexane to be the main products of the mercury photosensitized reaction of propylene and hydrogen. This supports Reaction (1) as a primary step, as does also the fact that the analogous reaction with ethylene is known to proceed with an activation energy probably less than 5 kcal. (3, 9). Reaction (2) might be expected since the corresponding reaction of methyl radicals with propylene to form methane and allyl is known to proceed readily with an activation energy of 3 kcal. (14). Formation of allyl, however, should lead to both

unsaturated and higher products. Since their formation was not appreciable, Reaction (2) does not appear to be of importance here. A chain-breaking step analogous to Reaction (3) has been found possible, although not favoured, in the reaction of hydrogen atoms with propane (11). In view of the strengthened C–C bond in propylene, the occurrence of Reaction (3) here would appear to be ruled out; this is supported by the fact that no unsaturated products were isolated.

Reaction (1) thus appears to be the main primary step. The non-occurrence of hexane, as contrasted with the results of the mercury photosensitized study, is due to the difference in pressure and hydrogen atom concentration between the two studies (11).

Secondary Reactions

The primary hydrogenation may be followed by the reactions postulated by Steacie and Parlee (11) in their study by the Wood–Bonhoeffer method of the reaction of hydrogen atoms with propane. Their mechanism at room temperature is:

$$C_3H_8 + H \longrightarrow C_3H_7 + H_2$$

$$C_3H_7 + H \longrightarrow CH_3 + C_2H_5 \qquad (4)$$

$$C_2H_5 + H \longrightarrow 2\ CH_3 \qquad (5)$$

$$CH_3 + H \longrightarrow CH_4 . \qquad (6)$$

In so far as hydrogen atoms are available, all steps in this mechanism should occur in the propylene reaction. However, there are two qualifying considerations:

(1) The above mechanism does not permit ethane formation at room temperature, except by radical recombination.

(2) The available hydrogen atom concentration is inadequate for all the above steps. On a stoichiometric basis, most of the available hydrogen atoms are consumed in Reaction (1). Evidently then, on this basis, Reaction (4) is the only one that will occur to an appreciable extent, and lower radicals, particularly methyl, might be expected to accumulate in the system. This suggests that some ethane formation may occur by recombination of methyl radicals. However, the nature of the products actually found precludes a high stationary concentration of lower radicals.

Hence, after propyl radical formation, the course of the propylene reaction must differ considerably from that of propane. The important features of the results may be explained tentatively by the following qualitative mechanism.

It is assumed that hydrogen atoms react with propylene to form active propyl radicals, since the reaction is approximately 40 kcal. exothermic†,

$$C_3H_6 + \dot{H} \longrightarrow C_3H_7^* . \qquad (7)$$

† *Values of 30, 93, and 103 kcal., respectively, being employed for the heat of formation of propane from propylene and hydrogen molecules (5), the C–H bond strength in propane, and the heat of dissociation of hydrogen.*

It is then suggested that active propyl radicals undergo at room temperature reactions possible only at higher temperatures for normal radicals.

Reactions of alkyl radicals with hydrogen molecules are known to occur at elevated temperatures (above 150° C.) and estimates of their activation energies vary from 9 to 15 kcal. (6, 7). Propane formation would thus occur by,

$$C_3H_7^* + H_2 \longrightarrow C_3H_8 + H,$$

for which E has been suggested to be about 13 to 14 kcal. (9). Alternative mechanisms for the formation of propane do not appear important. The reaction,

$$C_3H_7 + H \longrightarrow C_3H_8 \qquad (8)$$

has been shown not to occur (8). Some propane formation could occur by disproportionation of propyl radicals and lower radical recombination.

Since propyl radicals are energy-rich, they may also be expected to decompose at lower temperatures. Reactions of this type normally occur only at temperatures above 150° C. (10, 11). The following reactions should then take place:

$$C_3H_7^* \longrightarrow C_2H_4 + CH_3 \qquad (9)$$

$$C_2H_4 + H \longrightarrow C_2H_5^* \qquad (10)$$

$$C_2H_5^* + H_2 \longrightarrow C_2H_6 + H. \qquad (11)$$

Addition of hydrogen atoms to ethylene is assumed to give rise to an active ethyl radical. This would explain the formation of ethane at room temperature. Ethylene was not found in the products except for a trace in one run at 100° C., but it is known that Reaction (10) is very fast (4) and ethylene might not survive.

An examination by the Wood–Bonhoeffer method of the reaction of hydrogen atoms with ethylene over a range of hydrogen atom concentration would be of value for a detailed re-examination of the somewhat contentious mechanism of this reaction.

The above reactions will be accompanied by atomic cracking reactions such as (4) and (5). It is conceivable that active lower radicals might result from atomic cracking of active propyl radicals, as, for example,

$$C_3H_7^* + H \longrightarrow C_2H_5^* + CH_3,$$

followed by Reaction (11).

Formation of methyl radicals from ethyl by atomic cracking will evidently be reduced by removal of ethyl with ethane formation. However, the equality or preponderance of ethane formation, over methane, particularly if hydrogen atoms are produced as postulated, remains unexplained, unless it results from methyl radical recombination.

Formation of methane by the reaction

$$2\,CH_3 + H_2 \longrightarrow 2\,CH_4$$

has been postulated (12, 13). Occurrence of analogous reaction with ethyl would account for the more prominent features of the present results, but it

is difficult on the basis of available evidence to assess the probability of such a mechanism.

In the single run at slow propylene flow rate virtually no propane was formed, the amount of methane formation increasing very markedly and ethane formation but slightly. This result is readily interpreted as due to the preponderance of atomic cracking reactions in the presence of a large excess of hydrogen atoms.

Influence of Temperature

A noteworthy characteristic of the results is the temperature independence of the nature and proportions of the products. However, the two main reactions expected here, which normally occur only at higher temperatures (above 150° C.) and are primarily responsible for variation in products with temperature increase (10, 11, 16), are radical reaction with molecular hydrogen and propyl radical decomposition. The occurrence of these reactions with active radicals at room temperature, as postulated, would explain the temperature independence.

The Activation Energy of the Primary Step

The observed activation energy increases from 7.0 kcal. at 30° C. to 10.8 kcal. at 250° C. Similar increases in other studies have usually been ascribed to error in the assumed concentration of hydrogen atoms at higher temperatures, as a result of increased percentage reaction (10, 11). In the present study, however, the percentage reaction *decreased* with increase of temperature and this interpretation would not apply. The observed increase may be due, at least in part, to a decreased frequency factor brought about at higher temperatures by such effects as increased molecular rotation, etc. Since such activation energy increases are generally conceded to be fictitious, the value of 7 kcal. found here at room temperature is considered to be closest to the correct value.

A number of factors suggest that the value of 7 kcal. for propylene is too high. The steric factor was assumed to be 0.1 primarily for ease of comparison with other studies that have employed that value. This figure may be too large and a factor of 0.01 would give an E value around 5 kcal. Again, the value for E of 7 kcal. is calculated on the basis of the hydrogen atom concentration found in blank runs on hydrogen in the absence of propylene and any reaction. Since the amount of reaction was very high, the stationary hydrogen atom concentration must have been less than the values found. If the atom concentration were only 1%, the calculated activation energy would be reduced by several thousand calories.

The activation energy for the addition of hydrogen atoms to ethylene is considered to be around 5 kcal. (3, 9). Similarly it would appear that the activation energy of the primary step in the propylene reaction is also about, and possibly less than, 5 kcal.

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CANADIAN JOURNAL OF RESEARCH

VOLUME 21
1943
SECTION B

CANADA

Published by the
NATIONAL
RESEARCH COUNCIL
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SECTION B

INDEX TO VOLUME 21

Authors

Alexander, D. S.—See McRae, J. A.

Archibald, F. R.—See McRae, J. A.

Baer, E., Cushing, I. B., and Fischer, H. O. L.—On the synthesis of optically active β-phosphatidic acids, 119.

Blakers, A. L.—See Paul, E. B.

Boyd, M. L.—See Campbell, A. N.

Campbell, A. N. and Boyd, M. L.—The system: silver-nitrate–water, 163.

Chapman, R. A. and McFarlane, W. D.—A colorimetric method for the determination of fat-peroxides and its application in the study of the keeping quality of milk powders, 133.

Charlesworth, E. H.—See McRae, J. A.

Charlesworth, E. H., McRae, J. A., and MacFarlane, H. M.—The synthesis of 2-keto-cyclohexylsuccinic acid and related substances. II. Syntheses involving cyclohexanone, 55.

Cushing, I. B.—See Baer, E.

Davis, S. G.—See Rabinovitch, B. S.

Dewar, D. J.—See Munro, L. A.

Fischer, H. O. L.—See Baer, E.

Gallay, W. and Puddington, I. E.—
Sedimentation volumes and anomalous flow in lyophobic suspensions, 171.
The hydration of starch below the gelatinization temperature, 179.
The physical states of anhydrous sodium soaps, 202.
The effect of certain addition agents on the physical states of sodium soaps, 211.
Surface tension of sodium soap dispersions in mineral oils, 225.

Gallay, W., Puddington, I. E., and Tapp, J. S.—Wetting power in sodium-soap–mineral-oil systems, 230.

Gauvin, W. and Winkler, C. A.—
Use of the Haring cell for measuring addition agent concentration in electrolytic baths, 81.
Cathode surface changes in the presence of gelatin during electrodeposition of copper, 125.

Gertsman, S.—See Munro, L. A.

Giguère, P. A.—The refractive indices of hydrogen peroxide and its aqueous solutions, 156.

Harris, G. M., Schneider, W. G., and Thorvaldson, T.—The hydration of the aluminates of calcium. IV. Hydrothermal reactions of tricalcium aluminate and its hydrates, 65.

Hay, A. W. and Winkler, C. A.—The mercury photosensitized decomposition of *n*-butane, 149.

Johnson, H. and Thorvaldson, T.—The hydration of the aluminates of calcium. V. The hydrothermal decomposition products of tricalcium aluminate at 350° C., 236.

Klassen, J.—See Turral, W. T.

MacFarlane, H. M.—See Charlesworth, E. H.

McFarlane, W. D.—See Chapman, R. A.

McRae, J. A.—See Charlesworth, E. H.

McRae, J. A., Charlesworth, E. H., and Alexander, D. S.—The synthesis of 2-ketocyclohexylsuccinic acid and related substances. I. Syntheses involving cyclohexene oxide, 1.

McRae, J. A., Charlesworth, E. H., Archibald, F. R., and Alexander, D. S.—The synthesis of 2-ketocyclohexylsuccinic acid and related substances. III. Syntheses involving ethylene and propylene oxides, 186.

Manske, R. H. F.—
An alkaloid from *Menispermum canadense* L., 17.
The alkaloids of fumariaceous plants
XXXV. *Corydalis platycarpa* Makino, 13.
XXXVI. *Corydalis thalictrifolia* Franch., and the constitution of a new alkaloid, thalictrifoline, 111.
XXXVII. *Dactylicapnos macrocapnos* Hutchinson, 117.
The alkaloids of papaveraceous plants
XXXVIII. *Bocconia arborea* Wats., 140.

Manske, R. H. F. and Marion L.—
The alkaloids of *Lycopodium* species. III. *Lycopodium annotinum* L., 92.
The alkaloids of *Thermopsis rhombifolia* (Nutt.) Richards, 144.

Marion, L.—See Manske, R. H. F.

Marion, L.—Gelsemine. I. The degradation of gelsemine to 2 : 3-dimethyl-indole, 247.

May, W. G., Miners, K. A., and Spinks, J. W. T.—Preliminary examination of some Turner Valley crude oils, 73.

Miners, K. A.—See May, W. G.

Monteith, G.—See Munro, L. A.

Munro, L. A., Dewar, D. J., Gertsman, S., and Monteith, G.—The effect of gel water on catalytic activity. III. The decomposition of formic acid over alumina, 21.

Paul, E. B., Blakers, A. L., and Watson, R. W.—The rubber hydrocarbon of *Asclepias syriaca* L., 219.

Puddington, I. E.—See Gallay, W.

Rabinovitch, B. S., Davis, S. G., and Winkler, C. A.—The reaction of hydrogen atoms with propylene, 251.

Schneider, W. G.—See Harris, G. M.

Schneider, W. G. and Thorvaldson, T.—The hydration of the aluminates of calcium. III. The hydration of the 5 : 3, 1 : 1, and 3 : 5 calcium aluminates, 34.

Smedley, H.—See Turral, W. T.

Spinks, J. W. T.—See May, W. G.

Tapp, J. S.—See Gallay, W.

Thomas, J. F. J.—Inhibition of corrosion of aluminum and other metals in soda ash solutions, 43.

Thorvaldson, T.—See Harris, G. M., Johnson, H., and Schneider, W. G.

Turral, Wm. T., Klassen, J., and Smedley, H.—Froth flotation of rubber and resin components of milkweed and other plants that contain resins, rubber, balata, or related gummy substances, 195.

Wang, S. N. and Winkler, C. A.—The thermal decomposition of vinyl ethyl ether, 97.

Watson, R. W.—See Paul, E. B.

Winkler, C. A.—See Gauvin, W., Hay, A. W., Rabinovitch, B. S., and Wang, S. N.

SECTION B

INDEX TO VOLUME 21

Subjects

Acetaldehyde
Sensitized decomposition of, by vinyl ethyl ether, 103.
–vinyl-ethyl-ether mixtures, Effect of nitric oxide on rates of pressure change of, 105.

Acetic acid
Cyclohexanol-, γ-Lactone of, 8, 61.
Cyclohexanolbenzyl-, Lactone of, 10.
2-Ketocyclohexyl-,
Attempted preparation of lactam of, 9.
Lactone of, 9.
Synthesis of, 1, 8, 59.
2-Oxo-3-carboxytetrahydrofuran-3-, Preparation of, 189.
2-Oxohexahydrobenzofuran-3-, Preparation of, 7.
2-Oxohexahydroindole-3-, Preparation of, 8.
2-Oxotetrahydrofuran-3-, Preparation of, 189.

Addition agent(s)
concentration in electrolytic baths, Use of Haring cell for measuring, 81.
Effect of, on physical states of sodium soaps, 211.

Adlumidine, from Corydalis thalictrifolia, 115.

Alkaloid(s)
Degradation of gelsemine to 2 : 3-dimethylindole, 247.
F59 and F60 from Corydalis thalictrifolia, 111, 114, 115.
of fumariaceous plants
XXXV. Corydalis platycarpa Makino, 13.
XXXVI. Corydalis thalictrifolia Franch. and the constitution of a new alkaloid, thalictrifoline, 111.
XXXVII. Dactylicapnos macrocapnos Hutchinson, 117.
L8, L9, L10, L11, and L12 from Lycopodium annotinum, 92.
of Lycopodium species
III. Lycopodium annotinum L., 92.
of Menispermum canadense, 17.
P61 from Bocconia arborea, 140.
of papaveraceous plants
XXXVIII. Bocconia arborea, 140.
of Thermopsis rhombifolia (Nutt.) Richards, 144.

Allocryptopine from
Bocconia arborea, 140.
Dactylicapnos macrocapnos, 118.

Alumina, Decomposition of formic acid over, 21.

Aluminates of calcium, Hydration of the, 34, 65, 236.

Aluminum, and other metals, Inhibition of corrosion of, in soda ash solutions, 43.

Annotinine from Lycopodium annotinum, 93.

Anomalous flow in lyophobic suspensions, Sedimentation volumes and, 171, 179.

Apocynum androsaemifolium (dogbane)
Froth flotation of rubber and resin components of, 195, 199.

Asclepias syriaca (milkweed)
Froth flotation of rubber and resin components of, 195.
The rubber hydrocarbon of, 219.
X-ray diffraction patterns of rubber from, 220.

Aurotensine from Corydalis platycarpa, 16.

Balata, See under Froth flotation.

Benzofuran, 2-Oxohexahydro-, Preparation of, 9.

Bicuculline from Corydalis platycarpa, 15.

Bocconia arborea
Alkaloids from, 140.
Neutral nitrogenous compounds from,
Compound A, $C_{20}H_{17}O_4N$, 142.
Compound B, $C_{20}H_{15}O_4N$, 142.
Compound C, $C_{21}H_{23}O_5N$, 142.

***n*-Butane,** Mercury photosensitized decomposition of, 149.

Butyrolactone, γ-Hydroxy-α-benzyl-, Preparation of, 191.

Calcium, Hydration of aluminates of,
III. The hydration of the 5 : 3, 1 : 1, and 3 : 5 calcium aluminates, 34.
IV. Hydrothermal reactions of tricalcium aluminate and its hydrates, 65.
V. The hydrothermal decomposition products of tricalcium aluminate at 350° C., 236.

Catalysis, Effect of gel water on catalytic activity. III. The decomposition of formic acid over alumina, 21.

Cathode polarization in acid copper sulphate solutions, Measurement of, with a Haring cell, 81, 125.

Cathode surface changes in presence of gelatin during electrodeposition of copper, 125.

Cell, See Haring cell.

Chelerythrine, from Bocconia arborea, 140.

Colorimetry, Colorimetric method for determination of fat-peroxides, and its application in the study of keeping quality of milk powders, 133.

Cooling curves, Differential, of sodium stearate and sodium oleate, 202.

Copper
- Corrosion of, by soda ash solutions, Inhibition of, 43.
- Electrodeposition of,
  - Cathode polarization measurements with a Haring cell during, 81, 125.
  - Cathode surface changes in presence of gelatin during, 125.
  - Use of Haring cell for measuring addition agent concentration during, 81.

Corrosion of aluminum and other metals in soda ash solutions, Inhibition of, 43.

Corybulbine from Corydalis platycarpa, 15.

Corydaline from Corydalis platycarpa, 14.

Corydalis
- platycarpa, Alkaloids from, 13.
- thalictrifolia and the constitution of a new alkaloid, thalictrifoline, 111.

***l*-Corypalmine** from Corydalis thalictrifolia, 115.

Crude oils, Turner Valley, Preliminary examination of some, 73.

Cyclohexanone
- and ethyl bromomalonate
  - Attempted Grignard reaction with, 63.
  - Attempted Reformatsky reaction with, 62.
- and ethyl bromosuccinate. Attempted Reformatsky reaction with, 62.
- See under Succinic acid, 2-Keto-cyclohexyl-.

Cyclohexene oxide in synthesis of 2-keto-cyclohexylsuccinic acid and related substances, 1.

Cytisine and N-methyl-cytisine from Thermopsis rhombifolia, 147, 146.

Dactylicapnos macrocapnos, Alkaloids from, 117.

Dauricine
- Degradation of, 18.
- from Menispermum canadense, 17.

Density measurements on sodium stearate and sodium oleate, 202, 211.

Dilatancy of starch suspensions, 179.

Dispersion constant of hydrogen peroxide, from refraction data, 161.

Dispersions
- Effect of certain addition agents on physical states of sodium soap, 211.
- Surface tension of sodium soap dispersions in mineral oils, 225.
- Wetting power in sodium-soap–mineral-oil systems, 230.
- See also Lyophobic suspensions.

Distillation, Preliminary examination of some Turner Valley crude oils, 73.

Dogbane, See Apocynum androsaemifolium.

Duralumin, Corrosion of, by soda ash solutions, Inhibition of, 43.

Electrodeposition of copper, Cathode surface changes in presence of gelatin during, 125.

Electrolysis, See Copper, Electrodeposition of.

Ethylene, Sensitized polymerization of, by vinyl ethyl ether, 104.

Ethylene oxide, See under Succinic acid, 2—Ketocyclohexyl-.

Fat-peroxides in milk powder, Colorimetric method for determination of, 133.

Ferric oxide, Sedimentation volumes of, 171.

Flotation, See Froth flotation.

Flow, See Anomalous flow.

Formic acid, Decomposition of, over alumina, 21.

Froth flotation of rubber and resin components of milkweed and other plants that contain resins, rubber, balata, or related gummy substances, 195.

Furan
2-Oxo-3-benzyltetrahydro-, Preparation of, 191.
2-Oxo-3-carbethoxy-3-benzyltetrahydro-, Preparation of, 191.
2-Oxo-5-methyltetrahydro-, Preparation of, 191.

Gelatin
Cathode surface changes in the presence of, during electrodeposition of copper, 125.
Effect of, on cathode polarization in acid copper sulphate solutions, 81.

Gelatinization temperature, Hydration of starch below the, 179.

Gelsemine. I. The degradation of gelsemine to 2 : 3-dimethyl-indole, 247.

Gel water, Effect of, on decomposition of formic acid over alumina, 21.

Glue concentration of an electrolyte, Control of, with a Haring cell, 81.

Glycerol, Effect of, on
physical states of sodium soaps, 211.
surface relations between sodium soaps and mineral oils, 225, 231.

Glycerol
d(+) Acetone, Synthesis of optically active β-phosphatidic acids with, 119.
l(−)α-Benzoyl-, 120.
α′-Trityl-α-benzoyl-, 121.
α′-Trityl-*l*-α-benzoyl, 121.

β-Glycerophosphoric acid, Potassium salt,
γ-Benzoyl-, 122.
α-Trityl-α-benzoyl-, 122.
α′-Trityl-*l*-α-benzoyl-, 122.

Goat's-beard, See Tragopogon pratensis.

Grignard reaction, Attempted, with cyclohexanone and ethyl bromomalonate, 63.

Haring cell, Use of, for measuring addition agent concentration in electrolytic baths, 81.

Heat of wetting of dried starches, 184.

Hydration
of aluminates of calcium
III. The hydration of the 5 : 3, 1 : 1, and 3 : 5 calcium aluminates, 34.
IV. Hydrothermal reactions of tricalcium aluminates and its hydrates, 65.
V. The hydrothermal decomposition products of tricalcium aluminate at 350° C., 236.
capacity of starch, Effect of drying on, 182.
of starch below the gelatinization temperature, 179.

Hydrogen atoms, Reaction of, with propylene, 251.

Hydrogen peroxide and its aqueous solutions, Refractive indices of, 156.

Hydrothermal reactions
Hydrothermal decomposition products of tricalcium aluminate at 350° C., 236.
Hydrothermal treatment of the 5 : 3, 1 : 1, and 3 : 5 calcium aluminates, 34.
of tricalcium aluminate and its hydrates, 65.

Indole, 2 : 3-Dimethyl-, Degradion of gelsemine to, 247.

Inhibition of corrosion of aluminum and other metals in soda ash solutions, 43.

Iron, Galvanized, Corrosion of, by soda ash solutions, Inhibition of, 43.

Isocorydine from Corydalis platycarpa, 16.

***l*-Isocorypalmine** from Corydalis platycarpa, 16.

Keeping quality of milk powders, Colorimetric method for determination of fat-peroxides and its application to study of, 133.

Kinetics, Thermal decomposition of vinyl ethyl ether, 97.

Lactuca spicata (wild lettuce), Froth flotation of rubber and resin components of, 195, 199.

Latex, Milkweed
Preparation of rubber from, 220.
Properties of, 220.
Resin content of, 222.
X-ray diffraction patterns of rubber from, 220.
See also Asclepias syriaca.

Lettuce, Wild, See Lactuca spicata.

Luteanine, Identity of, with isocorydine, 13.

Lycopodine from Lycopodium annotinum, 95.

Lycopodium annotinum, Alkaloids of, 92.

Lycopodium species, Alkaloids of, III. Lycopodium annotinum, 92.

Lyophobic suspensions, Sedimentation volumes and anomalous flow in, 171.

Magnesium oxide, Sedimentation volumes of, 171.

Malonic acid
Bromo-, Ethyl ester, and cyclohexanone
Attempted Grignard reaction with, 63.
Attempted Reformatsky reaction with, 62.
2-Ketocyclohexyl-
Lactam of, Attempted preparation of, 10.
Synthesis of, 1, 9.

Menispermum canadense, Dauricine from, 17.

Mercury photosensitized decomposition of *n*-butane, 149.

Meso-corydaline from thalictrifoline, 114.

Milk powders, Colorimetric method for determination of fat-peroxides in, 133.

Milkweed, See Asclepias syriaca.

Mineral oil(s)
Effect of, on physical states of sodium soaps, 211.
–sodium soap dispersions
Surface tension of, 225.
Wetting power in, 230.
See also Crude oils.

Molecular constants of hydrogen peroxide from refraction data, 161.

Nitric oxide, Effect of, on rates of pressure change of vinyl-ethyl-ether–acetaldehyde mixtures, 105.

Obscurine from Lycopodium annotinum, 93.

Oils, See Crude oils and Mineral oils.

Oleic acid, sodium salt,
Density measurements and differential cooling curves of, 202.
Effect of glycerol and mineral oils on the physical states of, 211.
Surface tension of dispersions of, in mineral oils, 225.
Wetting power in dispersions of, in mineral oils, 230.

Optically active β-phosphatidic acids, Synthesis of, 119.

Oxidation of thalictrifoline, 113.

Oxidative rancidity, in milk powder, Colorimetric method for determination of, 133.

Palmatine, *l*-Tetrahydro-, from Corydalis platycarpa, 14.

Papaveraceous plants, Alkaloids of, 140.

β-Phosphatidic acids, Optically active, Synthesis of, 119.

Phosphoric acid, Glycerol ester, See Glycerophosphoric acid.

Photosensitized reactions, Mercury photo, sensitized decomposition of *n*-butane-149.

Plants
Alkaloids of,
See Bocconia arborea, Corydalis platycarpa, C. thalictrifolia, Dactylicapnos macrocapnos, Lycopodium annotinum, Menispermum canadense, and Thermopsis rhombifolia.
Froth flotation of rubber and resin components of milkweed and other, 195.
Rubber hydrocarbon of Asclepias syriaca, 219.

Polarizability of hydrogen peroxide, from refraction data, 161.

Polarization, Cathode, during electrodeposition of copper, Measurement of, with Haring cell, 81, 125.

Polymerization of ethylene, Sensitized, by vinyl ethyl ether, 104.

Propionic acid
2-Ketocyclohexyl-β-phenyl-, Attempted preparation of, 60.
2-Oxo-5-methyltetrahydrofuran-3-, Preparation of, 192.
2-Oxotetrahydrofuran-, Preparation of, 190.

α-Propionic acid
Cyclohexanol-, γ-Lactone of, 11, 62.
2-Ketocyclohexyl-, Preparation of, 11, 60.

Propylene, Reaction of hydrogen atoms with, 251.

Propylene oxide, See under Succinic acid, 2-Ketocyclohexyl-.

Protopine from
Bocconia arborea, 141.
Corydalis platycarpa, 16.
Corydalis thalictrifolia, 115.
Dactylicapnos macrocapnos, 117.

Pyrolysis of vinyl ethyl ether, 97.

Rancidity, Oxidative, in milk powders, Colorimetric method for determination of, 133.

Reformatsky reaction(s)
Attempted, with cyclohexanone and
ethyl bromomalonate, 62.
ethyl bromosuccinate, 62.
with cyclohexanone and
ethyl bromoacetate, 61.
ethyl α-bromopropionate, 62.

Refractive index of hydrogen peroxide and its aqueous solutions, 156.

Resin–rubber components of milkweed and other plants, 195, 220.
Froth flotation of, 195.

Rhombifoline, An alkaloid from Thermopsis rhombifolia, 147.

Rhombinine, An alkaloid from Thermopsis rhombifolia, 147.

Rubber
hydrocarbon of Asclepias syriaca, 219.
–resin components of milkweed, Froth flotation of, 195.

Sedimentation volumes
and anomalous flow in lyophobic suspensions, 171.
of magnesium oxide, ferric oxide, and talc, 171.
of starch, 171, 179.

Silicates, Commercial, Inhibitive action of, on corrosion of aluminum, duralumin, copper, tin plate, and galvanized iron by soda ash solutions, 43.

Silver-nitrate–water system, 163.

Soap(s), Sodium
Anhydrous, Physical states of, 202.
dispersions in mineral oils, Surface tension of, 225.
Effect of certain addition agents on physical states of, 211.
–mineral oil systems, Wetting power in, 230.

Soda ash, See Sodium carbonate.

Sodium carbonate solutions, Inhibition of corrosion of aluminum and other metals in, 43.

Sodium fluosilicate, Inhibitive action of, on corrosion of aluminum and other metals by soda ash solutions, 43.

Sodium silicates, Inhibitive action of, on corrosion of aluminum and other metals by soda ash solutions, 43.

Solubility curve, system silver-nitrate–water, 163.

Sonchus arvensis (sow-thistle), Froth flotation of rubber and resin components of, 195, 200.

Sow thistle, See Sonchus arvensis.

Specific refraction of hydrogen peroxide, 161.

Starch(es)
Dried, Heat of wetting of, 184.
Hydration of, below the gelatinization temperature, 179.
Sedimentation volumes of, 171, 179.
suspensions, Dilatancy of, 179.

Stearic acid, sodium salt,
Density measurements and differential cooling curves of, 202.
Effect of glycerol and mineral oils on physical states of, 211.
Surface tension of dispersions of, in mineral oils, 225.
Wetting power in dispersions of, in mineral oils, 230.

Stedman columns, Distillation of Turner Valley crude oils in, 73.

Stylopine from
Corydalis thalictrifolia, 114.
Dactylicapnos macrocapnos, 118.

***dl*-Stylopine** from Corydalis platycarpa, 15.

Succinamide, α-(β-Hydroxyethyl)-, Preparation of, 190.

Succinic acid
Bromo-, ethyl ester
Attempted Reformatsky reaction with cyclohexanone and, 62.
Modified method of preparation, 59.
2-Ketocyclohexyl-, and related substances, Synthesis of,
I. Syntheses involving cyclohexene oxide, 1.
II. Syntheses involving cyclohexanone, 55.
III. Syntheses involving ethylene and propylene oxides, 186.

Succinic lactone, Cyclohexanol-, 6.

Sulphuric acid, Effect of, on cathode polarization during electrodeposition of copper, 83.

Surface tension of sodium soap dispersions in mineral oils, 225.

Suspensions, See Lyophobic suspensions and Dispersions.

Talc, Sedimentation volumes of, 171.

Temperature
–concentration diagram of system silver-nitrate–water, 163.
–density relations of
anhydrous sodium soaps, 202.
sodium soaps containing addition agents, 211.

Temperature—*concluded*
Effect of, on
cathode polarization during electrodeposition of copper, 84.
sedimentation volume and dilatancy of starch, 181.
Gelatinization, Hydration of starch below the, 179.

Thalictrifoline (alkaloid F58)
from Corydalis thalictrifolia, 113.
dl-, 113.
hydrochloride, Dehydro-, 112.
Meso-corydaline from, 114.
Oxidation of, 113.

Thermal decomposition of
4 : 3 : 3 calcium hydroaluminate, 242.
vinyl ethyl ether, 97.

Thermopsine from Thermopsis rhombifolia, 146.

Thermopsis rhombifolia
Alkaloids from, 144.
Neutral non-nitrogenous compounds from,
Compound A ($C_{19}H_{20}O_{10}$), 145.
Compound B ($C_{22}H_{16}O_8$), 145.

Tin plate, Corrosion of, by soda ash solutions, Inhibition of, 43.

Tragopogon pratensis (goat's-beard),
Froth flotation of rubber and resin components of, 195, 199.

Tricalcium aluminates, Hydration of, 34, 65, 236.

Turner Valley crude oils, Preliminary examination of some, 73.

γ-Valerolactone, Preparation of, 191.

Vinyl ethyl ether
Sensitized decomposition of acetaldehyde and ethylene by 103, 104.
Thermal decomposition of, 97.

Water content of gels, Effect of, on decomposition of formic acid over alumina, 21.

Water–silver-nitrate system, 163.

Wetting
Heat of, of dried starches, 184.
power in sodium-soap–mineral-oil systems, 230.

Wild lettuce, See Lactuca spicata.

X-ray
diffraction patterns of rubber from milkweed latex, 220.
powder patterns of 4 : 3 : 3 calcium hydroaluminate, Data obtained from, 243.

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